Combining HDC and CWPO for the removal of *p*-chloro-*m*-cresol from water under ambient-like conditions

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A B S T R A C T

Catalysts supported on aluminium pillared clays (Al-PILCs) using Fe and Pd or Rh as active phases have been prepared and tested for a two-step treatment of *p*-chloro-*m*-cresol (PCMC) in water by catalytic hydrodechlorination (HDC) followed by catalytic wet peroxide oxidation (CWPO) under ambient-like conditions (25 °C, 1 atm). Both processes were first studied independently. HDC was investigated with Pd and Rh monometallic catalysts as well as Pd-Fe and Rh-Fe bimetallic ones. The bimetallic Pd-Fe catalyst showed the best performance, allowing complete dechlorination in less than 1 h reaction time. On the other hand, CWPO of PCMC with a monometallic Fe catalyst allowed complete conversion of that pollutant but with only about 33% reduction of total organic carbon (TOC) after 4 h. Then, a two-step approach consisting in HDC of PCMC followed by CWPO has been tested for the first time in two different ways. The first one used a Pd-Fe bimetallic catalyst in both steps while in the second approach monometallic Pd and Fe catalysts were used for HDC and CWPO, respectively. The HDC in alkaline medium allowed reducing significantly Fe leaching. This second approach yielded complete dechlorination followed by higher mineralization (>55%) with better efficiency of H_2O_2 consumption.

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1. Introduction

Chlorinated organic compounds are commercially important chemicals. Among them, chlorinated cresols, as *p*-chloro-*m*-cresol (PCMC) are widely used as antiseptics and preservative agents in resin, herbicides, pharmaceuticals and surfactants manufacture. Wastewater from these industries, besides coal-conversion units and petrochemicals, contain high concentration of cresols, which have been classified by US-EPA as persistent and toxic. In particular, PCMC has strong antimicrobial effect and is used in adhesives, emulsions, paints, inks, textile and leather goods [1]. This compound has received special attention due to its high toxicity and its possible disrupting endocrine effect [2,3]. PCMC has been also classified by several studies into the "pharmaceuticals and personal care products (PPCPs)" group, which mainly consists of prescription drugs, fragrances, sunscreens and antiseptics, where PCMC is also frequently used [4,5]. PCMC pollution can be found in surface [6], ground [7] and drinking water [8]. Among the potential

solutions for the removal of organochlorinated pollutants from water, catalytic hydrodechlorination (HDC) has received increasing attention. It involves the reductive breakdown of the C—Cl bond by highly reactive atomic hydrogen, and has proved to be effective under ambient-like conditions with different chlorinated compounds such as polychlorinated benzenes, chlorophenols (CPs), PCBs or dioxins, leading to their transformation into much less harmful species [9,10]. Advanced oxidation processes (AOPs), based on the action of hydroxyl radicals, can be used for the elimination of the remaining organic matter. Among them, the use of catalytic wet peroxide oxidation (CWPO) or heterogeneous Fenton oxidation has been widely studied in the last decade [11]. Xu and Wang [12] reported on the degradation of PCMC by Fenton-like oxidation with zero-valent iron/H_2O_2 system, achieving complete conversion of the initial PCMC (100 mg/L) and 63% TOC removal at 30 °C. However, it has been proved that Fenton oxidation of chloroaromatic compounds in aqueous phase can lead to the formation of highly toxic intermediates [13,14]. Therefore, the application of HDC prior to the oxidation treatment can avoid the formation of those toxic chlorinated by-products. To the best of our knowledge, combined HDC and CWPO has been studied only for the abatement of chlorophenols with bimetallic and monometallic catalysts [15,16]. In those studies, phenol and cyclohexanone were the main

reaction products from HDC. Further oxidation of phenol is easier than that of cyclohexanone and, therefore, it is advisable to avoid a deeper hydrogenation in the HDC step [17].

Different catalysts have been tested for that combined approach, being commonly based on precious and transition metals as active phases. As supports have been used alumina [15], carbon [18,19] and pillared clays [20] among others. The most used active phases supported on pillared clays have been Fe and Cu for CWPO and Pd and Rh for HDC. Recently, precious metals supported on pillared clays have been reported as stable and very active catalysts for the HDC of chlorophenols [21], chloronitrobenzene and chloroaniline [22]. Likewise, catalysts based on Fe supported on pillared clays have shown high activity in the CWPO of 4-chlorophenol [23]. Among the different catalytic supports studied for oxidation processes, pillared clays represent only around 7% but the interest on these materials has increased substantially in the last years [20].

The current work investigates the combination of HDC followed by CWPO for the treatment of PCMC in aqueous phase with catalysts based on Pd, Rh and Fe as active phases supported on Al-PILCs. Firstly, HDC and CWPO are studied independently, analyzing the reaction pathways of PCMC degradation in each process. Based on those results, the application of a sequential HDC−CWPO approach will be investigated in this work following two different ways: (i) using a single bimetallic catalyst for both processes and (ii) using different monometallic catalysts for each step of the sequential treatment.

2. Materials and methods

2.1. Catalysts preparation

The catalysts tested were prepared using a purified-grade bentonite supplied by Fisher Scientific Company as raw material which contains 3.8% of Fe. Pd and Rh monometallic catalysts (1 wt.%) used for HDC were synthesized using Al-PILC as support, which was prepared following the procedure described elsewhere [24]. Both catalysts, referred as Pd-1 and Rh-1, respectively, were prepared by impregnation of Al-PILC with $PdCl_2$ and $RhCl_3$ salts using acidic (HCl) solutions [21]. The wet solid was dried for 2 h at room temperature followed by 14 h at 110 °C and finally, calcined in air atmosphere for 2 h at 500 °C, reached at 2 °C/min heating rate.

Fe monometallic catalysts used in CWPO were prepared by two different methods. In the first one (named AlFe), Fe was introduced by pillaring the raw bentonite with a mixture of Al-Fe using as precursors $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$. The aging temperature of the pillaring solution was 25 °C according to the preparation method described in a previous work [25]. The second monometallic Fe catalysts (IMPFe) was prepared by wet impregnation of Al-PILC with a $Fe(NO_3)_3$ solution. The wet solids from both preparation procedures were dried for 2 h at 25 °C and 14 h at 110 °C and then calcined for 2 h at 400 °C. The iron load of the resulting catalysts was around 7 wt%.

The bimetallic Pd-Fe and Rh-Fe catalysts used in HDC and in the combined HDC-CWPO experiments, were prepared by wet impregnation of the aforementioned Fe-monometallic catalysts with acidic $PdCl_2$ or $RhCl_3$ solutions. The resulting samples were then dried for 2 h at 25 °C and 14 h at 110 °C and then calcined for 2 h at 500 °C. The nominal precious metal load was adjusted to 1 wt%. The bimetallic catalysts were denoted according to the method used for the incorporation of Fe (e.g. AlFe- or IMPFe-) and to the precious metal (e.g. AlFe-Rh and IMPFe-Pd).

All the catalysts containing noble metals (Pd-1, Rh-1, AlFe-Pd, AlFe-Rh, IMPFe-Pd and IMPFe-Rh) were reduced under H_2 flow (50 NmL/min) at 90 °C during 2 h before the HDC experiments. A N_2 flow (35 NmL/min) was then passed to clean the catalyst surface.

2.2. Catalyst characterization

A Micromeritics Tristar 3000 apparatus was used to obtain the N_2 adsorption-desorption isotherms at −196 °C. The samples were previously outgassed at 160 °C and 5×10^{-3} Torr for 16 h. Specific areas were obtained according to the BET method. The metal content of the catalysts was measured by X-ray fluorescence with a TXRF EXTRA-II spectrometer (Rich & Seifert, Germany) after digestion of the samples by acid treatment (aqua regia mixture) at 100 °C. The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm coupled with an energy-dispersive X-ray spectrometer (EDXS; INCA x-sight, Oxford Instruments) used for chemical elemental analysis. Iron species in the bentonite and the fresh and reduced catalysts were also identified by Mössbauer spectroscopy. Mössbauer spectra at room temperature and −196 °C were recorded in triangle mode using a conventional spectrometer with $^{57}Co(Rh)$ source. The spectra were analyzed by a non-linear fit using the NORMOS program [26] and the energy calibration was made using a α-Fe (6 μm) foil.

2.3. Catalytic experiments

2.3.1. Hydrodechlorination

HDC of PCMC (100 mg/L initial concentration) was carried out at 25 °C and 1 atm in jacketed glass reactors (1.1 L capacity) operating in batch, under continuous stirring (360 rpm). The selected catalyst (1 g/L, particle size lower than 100 μm) was added to 1 L of an aqueous PCMC solution and H_2 flow (50 NmL/min) was continuously fed to the reactor.

2.3.2. CWPO and Fenton oxidation experiments

CWPO of PCMC was studied using AlFe and IMPFe catalysts (1 g/L, particle size lower than 100 μm). The experiments were carried out at 25 °C in the same reactor and with the same volume and stirring velocity used in the HDC of PCMC. Unless otherwise indicated, the initial concentration of PCMC was set at 100 mg/L, the catalyst concentration at 1 g/L and the H_2O_2 dose at the stoichiometric (380 mg/L). The initial pH of the reaction medium was adjusted to 3.5 with diluted HNO_3.

To learn more on the species formed upon CWPO of PCMC an additional experiment was carried out at higher initial concentration (1000 mg/L) and low H_2O_2 dose (20% of the stoichiometric). The same was done with m-cresol. The oxidation of PCMC and m-cresol by homogeneous Fenton oxidation under the same conditions previously described for CWPO was also studied to gain further insights on the reaction pathways of PCMC oxidation. The Fe^{3+} dose was 10 mg/L [14,27].

2.3.3. Sequential HDC-CWPO with single bimetallic catalyst

The treatment of PCMC (100 mg/L initial concentration) by sequential HDC-CWPO was carried out under ambient-like conditions (25 °C) using the same bimetallic catalyst (IMPFe-Pd, 1 g/L, particle size lower than 100 μm) for both processes. In the HDC step H_2 was continuously fed to the reactor at 50 NmL/min. The initial pH of the reaction medium for the HDC step was adjusted to 10 in order to avoid iron leaching from the catalyst. After 30 min of HDC, the H_2 flow was stopped and the pH of the reaction medium was adjusted to 3.5 with HNO_3 (0.1 M). Then, the theoretical stoichiometric amount of H_2O_2 for complete oxidation of the reaction products quantified after the HDC step, was added to the reaction medium to start the CWPO process.

Table 1
Characterization of the starting bentonite, Al-PILC support and the catalysts prepared.

Sample	BET surface area (m^2/g)	External Area (m^2/g)	Micropore Volume (cm^3/g)	Fe content (wt%)	Pd content (wt%)	Rh content (wt%)
Bentonite	35	24	0.005	3.8	–	–
Al-PILC	215	70	0.060	3.4	–	–
Pd-1	162	62	0.043	3.4	1.00	–
Rh-1	156	55	0.044	3.4	–	0.98
AlFe	236	82	0.081	7.2	–	–
IMPFe	145	58	0.041	6.3	–	–
AlFe-Pd	177	82	0.057	7.4	0.98	–
AlFe-Rh	176	80	0.055	7.3	–	0.96
IMPFe-Pd	89	35	0.031	6.4	1.01	–
IMPFe-Rh	94	39	0.033	6.5	–	1.10

2.3.4. Sequential HDC-CWPO with different monometallic catalysts in each step

This HDC-CWPO experiment was performed using the Pd-1 and AlFe catalysts for the HDC and CWPO steps, respectively. The operating conditions were the same as previously described (25 °C, 1 g/L catalyst, 100 mg/L initial PCMC concentration, 50 NmL/min H$_2$ for HDC and the stoichiometric amount of H$_2$O$_2$ for CWPO). After 30 min of HDC the catalyst was separated by filtration (PTFE 0.45 μm) and the pH was adjusted to 3.5 with HNO$_3$ (0.1 M). Then, the AlFe catalyst and H$_2$O$_2$ were added to start the CWPO step. Replicates of all the experiments were performed in order to check the reproducibility of the results obtained.

2.4. Analytical methods

The progress of the reactions was followed by periodically analyzing liquid samples extracted from the reactor. The concentration of the target compound, PCMC, was determined by HPLC using a diode-array detector (Prostar, Varian), a C$_{18}$ as stationary phase (Valco Microsorb-MW 100-5C$_{18}$) and a mixture of acetonitrile and water (1:1 v/v) as mobile phase. The same procedure was used to analyse the main HDC reaction product, *m*-cresol. The other products formed in the HDC reaction, 3-methyl-cyclohexanone and 3-methyl-cyclohexanol, were analyzed by GC/FID (GC 3900 Varian) using a 30 m length x 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. To identify the aromatic and condensation products obtained upon CWPO and Fenton experiments, the samples were extracted in *n*-hexane and then analyzed by Gas Chromatography (MS detector) with an electron impact ionization source (Saturn 2100T). Aqueous samples were also analyzed after the extraction with polydimethylsiloxane (PDMS) fibre. The capillary column used was a Factor Four, Varian (30 m length, 0.25 mm internal diameter). The dark brown solid formed upon homogeneous Fenton oxidation was separated using a nylon membrane filter of 0.45 μm pore size (Sigma-Aldrich). After drying, it was characterized by elemental analysis (LECO elemental analyzer) and Total Reflection X-Ray Fluorescence (Chemical Analysis Seifert EXTRA-II spectrometer). Short-chain organic acids from CWPO and chloride from both, HDC and CWPO, were quantified by ion chromatography (Metrohm 790 Personal IC) using a Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) as stationary phase and a 3.2 mM Na$_2$CO$_3$ aqueous solution as the mobile phase. Total Organic Carbon (TOC) was measured with a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H$_2$O$_2$ concentration was determined by colorimetric titration following the titanium sulfate method [28] using an UV 1603 Shimadzu UV/Vis spectrophotometer. Fe leached from the catalyst to the liquid phase was analyzed by the *o*-phenantroline method [29]. Replicates of the different reactions yielded raw data reproducibility better than ±5% in all the cases.

3. Results and discussion

3.1. Characterization of the catalysts

The values of the BET area and the metal content of the support and catalysts are given in Table 1. The catalysts prepared by pillaring of the raw bentonite with Al-Fe mixtures showed higher Fe contents as well as micropore volume and BET surface area. On the opposite, the impregnation method led to catalysts with lower surface area values, probably due to higher metal intrusion in the micropores upon impregnation. Also, the acid used in the impregnation of precious metals affects negatively to the Al pillars inside the basal spacing as observed in previous works with bimetallic catalysts [30,31].

The raw bentonite, Al and Al-Fe pillared clays and the most active bimetallic catalyst in the HDC reaction, IMPFe-Pd, were analyzed by Mössbauer spectroscopy in order to know the state of Fe in each material (Fig. 1). The starting bentonite and Al-PILC, both containing Fe, yielded spectra which can be interpreted as the combination of two quadrupole doublets. The hyperfine parameters are shown in Table 2, corresponding to Fe (III) and Fe (II). The bentonite presents Fe (II), possibly due to exchanged cations or isomorphic substitutions, and Fe (III). After calcination at 350 °C (Al-PILC synthesis) partial oxidation of Fe (II) to Fe (III) was observed. Complete oxidation of Fe (II) to Fe (III) occurred when the Al-Fe pillared clays were calcined at 400 °C in air. No change was observed in the oxidation state of Fe after reduction at 90 °C under H$_2$ flow. These results are in agreement with the obtained by other authors with Pt-Fe-PILCs, where the reduction of Fe took place at temperatures over 350 °C [32].

3.2. HDC of PCMC with Pd and Rh monometallic catalysts

The Pd and Rh monometallic catalysts tested allowed complete dechlorination of PCMC in relatively low reaction times (1 and 2 h for Rh-1 and Pd-1, respectively), as can be seen in Fig. 2. Dispersion values of 8.3% and 22% were obtained for Pd-1 and Rh-1 catalysts, respectively, in a previous work [21]. The curves in that figure indicate that both catalysts promote dechlorination to *m*-cresol in a first step, which is then partially converted into 3-methylcyclohexanone upon further hydrogenation in the

Table 2
Mössbauer parameters of the bentonite, AlPILC support and the catalysts.

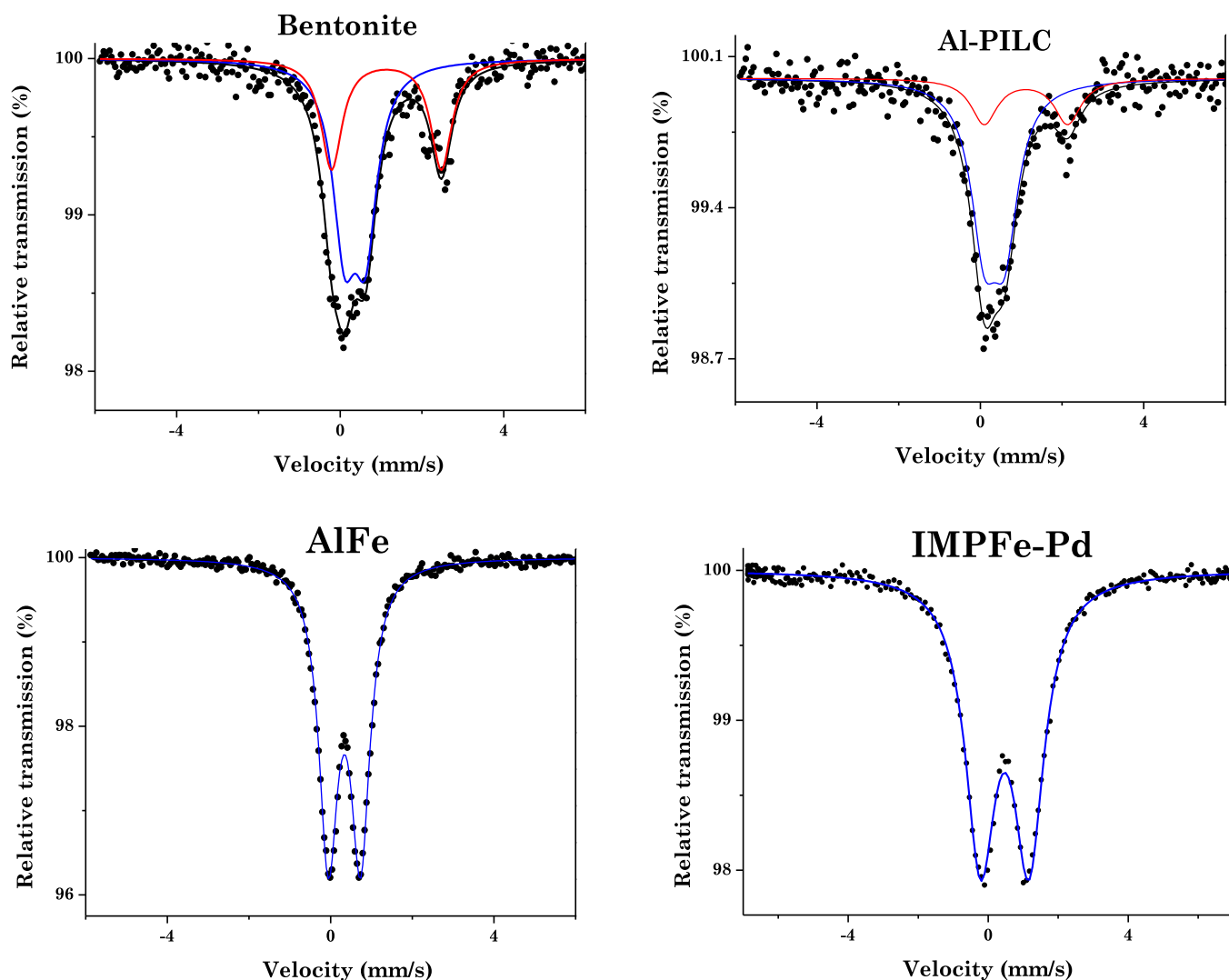| Spectrum	δ^a (mm/s)	QS(mm/s)	%Fe III	%FeII
Bentonite	0.37	0.51	63	
	1.14	2.68		37
AlPILC	0.34	0.5	76	
	1.11	2.04		24
AlFe	0.34	0.78	100	
IMPFe-Pd	0.34	0.81	100	
IMPFe-Pd red 90 °C	0.47	1.38	100	

^{a} Isomer Shifts relative to α-iron.

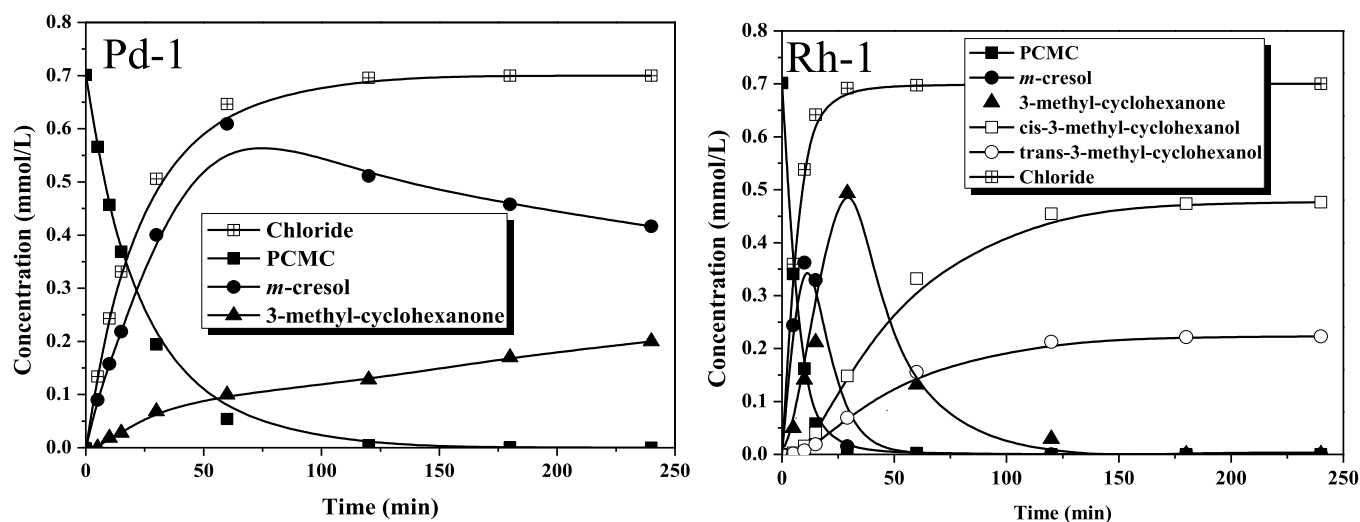**Fig. 1.** Mössbauer spectra of the raw bentonite, Al-pillared clay and the Fe-bearing catalysts prepared.
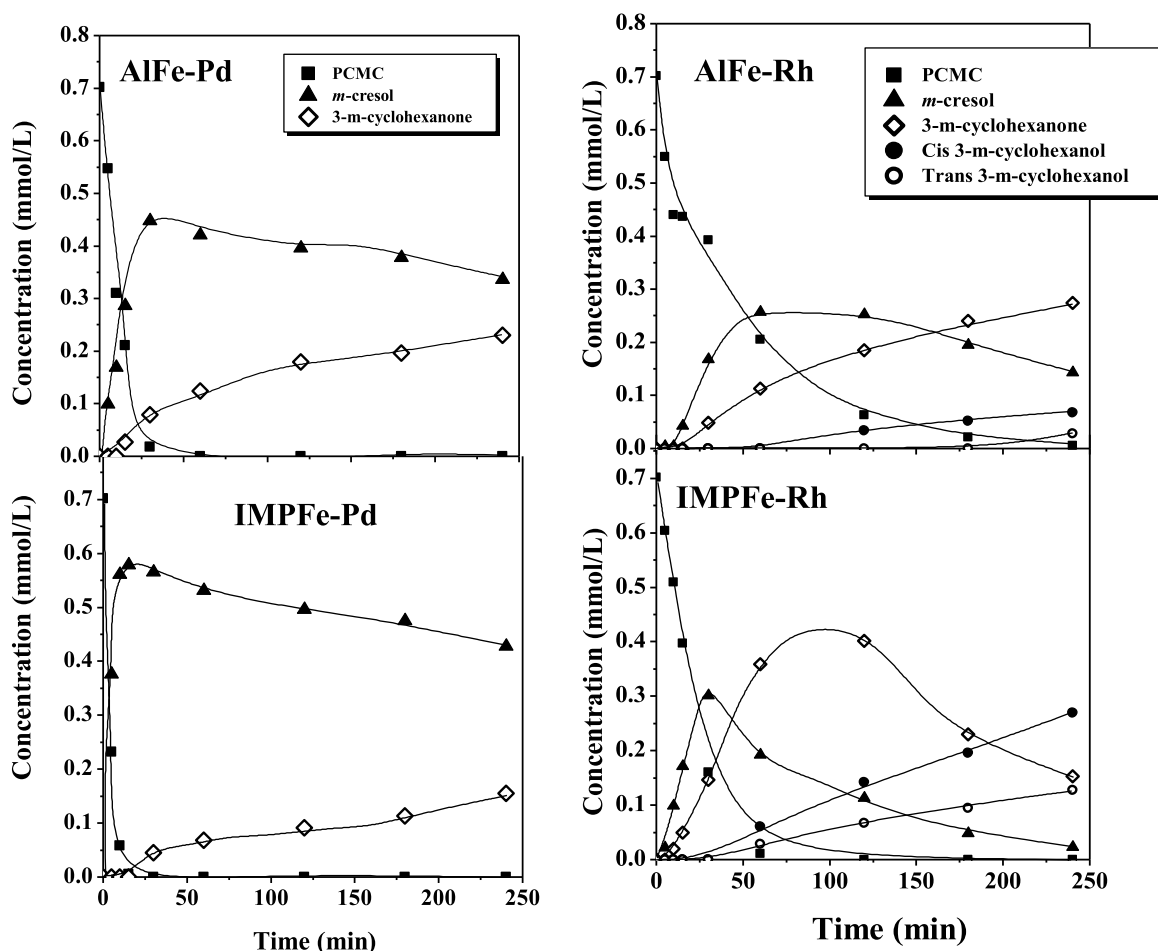

Fig. 2. HDC of PCMC with monometallic Pd-1 and Rh-1 catalysts (25 °C, 1 atm, $pH_0 = 6$, $Q_{H_2} = 50$ NmL/min, [catalyst]$_0$ = 1 g/L, [PCMC]$_0$ = 0.7 mmol/L).

case of the Pd catalyst. With the Rh one, the reaction pathway follows a more complex pattern where *m*-cresol is completely converted into 3-methylcyclohexanone which undergoes further hydrogenation to 3-methylcyclohexanol. The Rh catalyst showed higher dechlorination activity and also promoted a substantially deeper hydrogenation of the dechlorinated byproducts, in good

Fig. 3. HDC of PCMC with bimetallic Pd-Fe and Rh-Fe catalysts (25 °C, 1 atm, $pH_0 = 6$, $QH_2 = 50$ NmL/min, [catalyst]$_0$ = 1 g/L, [PCMC]$_0$ = 0.7 mmol/L).

agreement with previous studies dealing with HDC with Pd and Rh as active phases under ambient-like conditions [21,33–35]. The support and Fe-bearing catalysts were used in previous catalytic tests to discard any influence of the structural or added iron in the HDC process.

3.3. HDC of PCMC with bimetallic catalysts

The results obtained with the bimetallic catalysts are depicted in Fig. 3. The incorporation of iron enhanced quite significantly the dechlorination activity of the Pd catalyst while it barely affected to further hydrogenation. The effort was particularly important in the catalyst prepared by impregnation (IMP-Fe) where the initial rate of PCMC disappearance increased more than ten-fold (see Table 3). This result is in good agreement with the reported in previous works [15,36] and can be attributed to a higher dispersion of Pd nanoparticles favored by the interaction with iron. The mean

Pd nanoparticle size in the monometallic Pd-1 catalyst (Fig. 4a) was higher than the obtained for the bimetallic IMPFe-Pd catalyst, which contained Pd-Fe nanoparticles in all cases (Fig. 4b–d). Although to a lesser extent, Pd and Fe monometallic nanoparticles were also identified in the bimetallic catalyst as depicted in Fig. 4d and e. In previous works it was observed a relatively low metal dispersion in monometallic AlPILC-supported Pd catalysts with nanoparticle mean size around 10 nm and a wide size distribution [21,22]. The lower metal particle size showed by the bimetallic catalyst can be associated with the higher activity in the PCMC hydrodechlorination and the slightly lower for further hydrogenation of *m*-cresol to 3-methyl-cyclohexanone. This last result is consistent with the low hydrogenation activity of small Pd nanoparticles or Pd-Fe alloys reported by other authors [37].

On the opposite, the incorporation of iron led to a significant decrease of the HDC activity of the Rh-based catalysts. The dispersion of the active phase remained almost unchanged after iron addition with nanoparticle sizes within the range of 2–4 nm, similar to the observed for the monometallic catalysts [21]. This decrease of activity could be due to the interaction between of Rh and Fe.

The method used for Fe incorporation determines the availability of Fe on the catalyst surface, which is higher in the impregnated catalysts than in the pillared ones.

To learn on the stability of the bimetallic catalysts, the Fe leached to the reaction medium was analyzed at the end of the HDC experiments (Table 3). As observed, fairly similar concentrations of dissolved iron were measured regardless the accompanying metal (Pd or Rh) or the preparation method (AlFe, IMPFe). The amount of Fe leached corresponded to around a quarter of the ini-
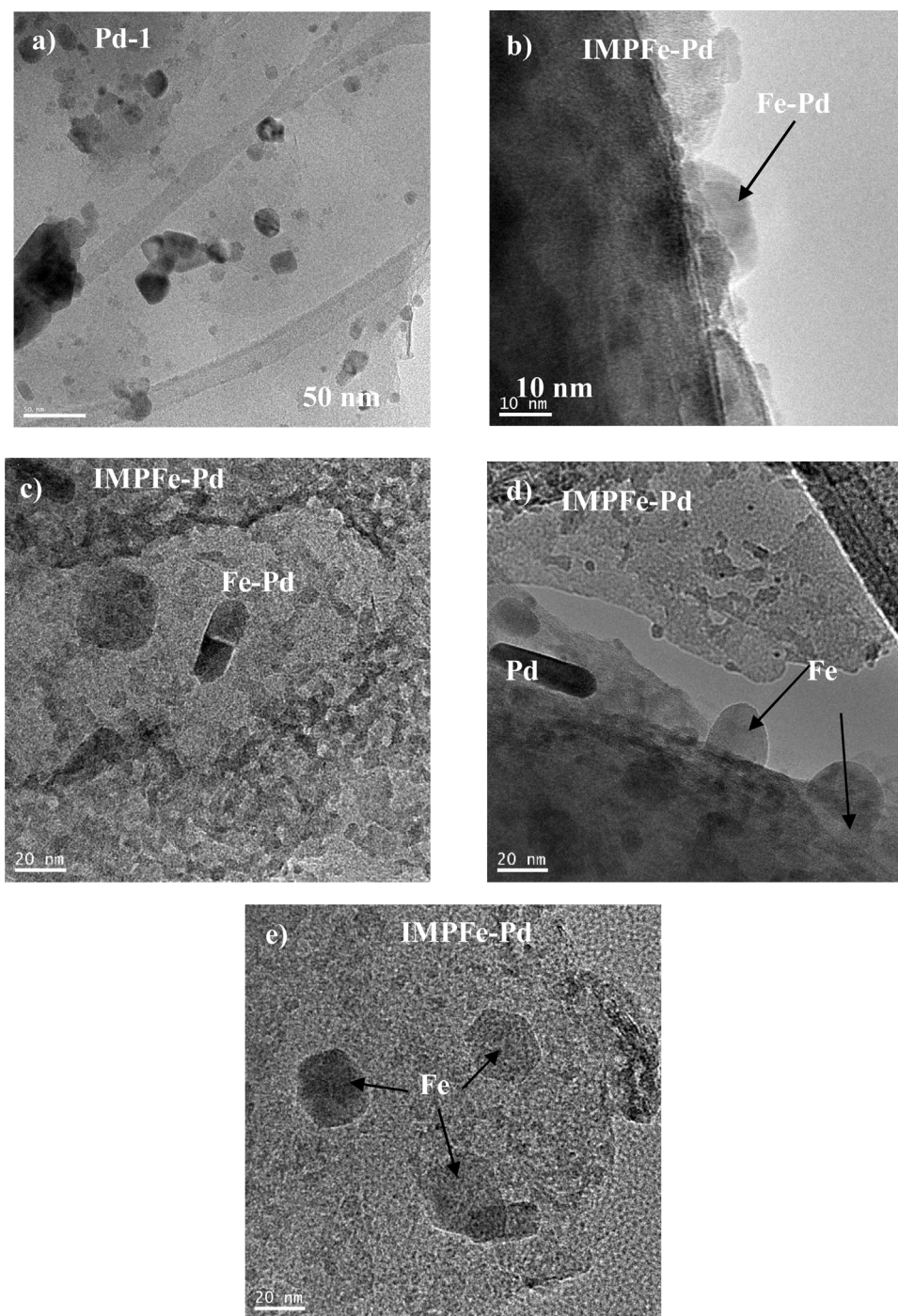
Table 3
Initial rate values of PCMC hydrodechlorination and Fe leaching upon 4 h reaction time (25 °C, 1 atm, $QH_2 = 50$ NmL/min [catalyst] = 1 g/L, [PCMC]$_0$ = 0.7 mmol/L).

Catalyst	Initial rates (mmol/min g$_{noblemetal}$)	Dissolved Fe (mg/L)
Pd-1	3.0	<0.1
Rh-1	10.0	<0.1
AlFe-Pd	8.3	16.9
AlFe-Rh	1.2	16.4
IMPFe-Pd	31.5	16.7
IMPFe-Rh	5.4	17.2
IMPFe-Pd (pH10)	33.6	3.5

Fig. 4. TEM images of the Pd-1 (a) and IMPFe-Pd (b, c, d and e) catalysts.

tial load in the catalysts. This Fe leaching can be related to the HCl produced upon HDC. To confirm this, an additional HDC experiment with the optimum catalyst IMPFe-Pd was carried out at pH 10 (NaOH) in order to neutralize the HCl generated. Notably, the amount of Fe leached was significantly lower (see Table 3), representing around 5% of the initial iron content. Furthermore, the HDC activity remained almost unchanged whereas further hydrogenation was significantly enhanced, leading to the same amounts of m-cresol and 3-methyl-cyclohexanone, ($\approx$0.3 mmol/L) at the end of the 4 h-experiment (Fig. 5). The closure of chlorine balance was always above 99% after the HDC with both mono and bimetallic catalysts. TXRF analyses of the effluents from 4-CP HDC confirmed the absence of dissolved Pd or Rh.

3.4. CWPO of PCMC with the AlFe catalyst

Fig. 6 shows the evolution of PCMC, m-cresol and chloride concentrations as well as TOC and H_2O_2 conversion upon CWPO of PCMC (100 mg/L initial concentration) with the AlFe catalyst at 25 °C. Complete conversion of PCMC was achieved after 2 h reaction time, but the TOC decreased only by 33% at the end of the 4 h-experiment. Therefore, important amounts of reaction by-products are remaining. Moreover, these must include chlorinated species since the chlorine balance closure was around 85%. H_2O_2 conversion was less than 50% after 4 h and some organic acids were identified (i.e. acetic, formic, malonic and oxalic) as in previous works on Fenton oxidation of PCMC [38] and cresols [39] as well
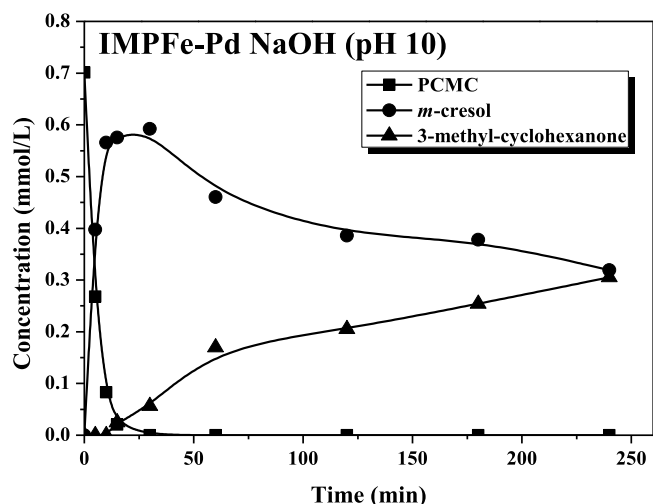
Fig. 5. HDC of PCMC with IMPFe-Pd in presence of NaOH (25 °C, 1 atm, $Q_{H_2} = 50$ NmL/min, [IMPFe-Pd] = 1 g/L, [PCMC]$_0$ = 0.7 mmol/L, stoichiometric NaOH dose respect to the maximum theoretical HCl produced).
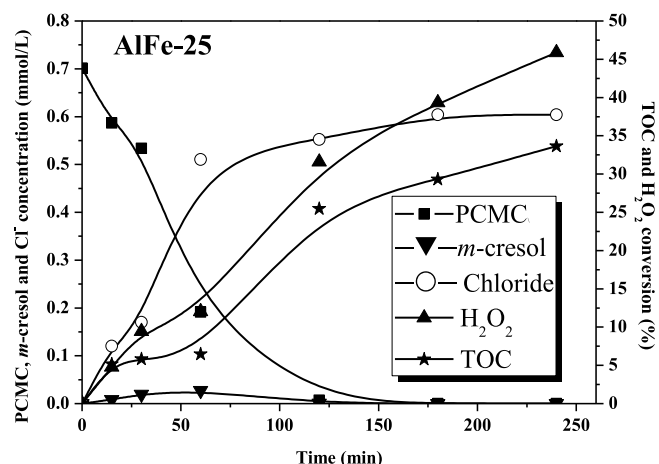

Fig. 6. CWPO of PCMC with AlFe25 (25 °C, 1 atm, [PCMC]$_0$ = 0.7 mmol/L, [catalyst] = 1 g/L, stoichiometric dose of H_2O_2).

as ozonation of these last [40]. The iron leached was very low, 1.1 mg/L, representing 1.5% of the initial Fe in the catalyst.

The formation of highly toxic chlorinated by-products represents an important drawback regarding the direct application of CWPO for the degradation of chlorine-bearing organic pollutants in water [15]. The above results indicate that non-identified chlorinated intermediates are formed upon CWPO of PCMC. To learn
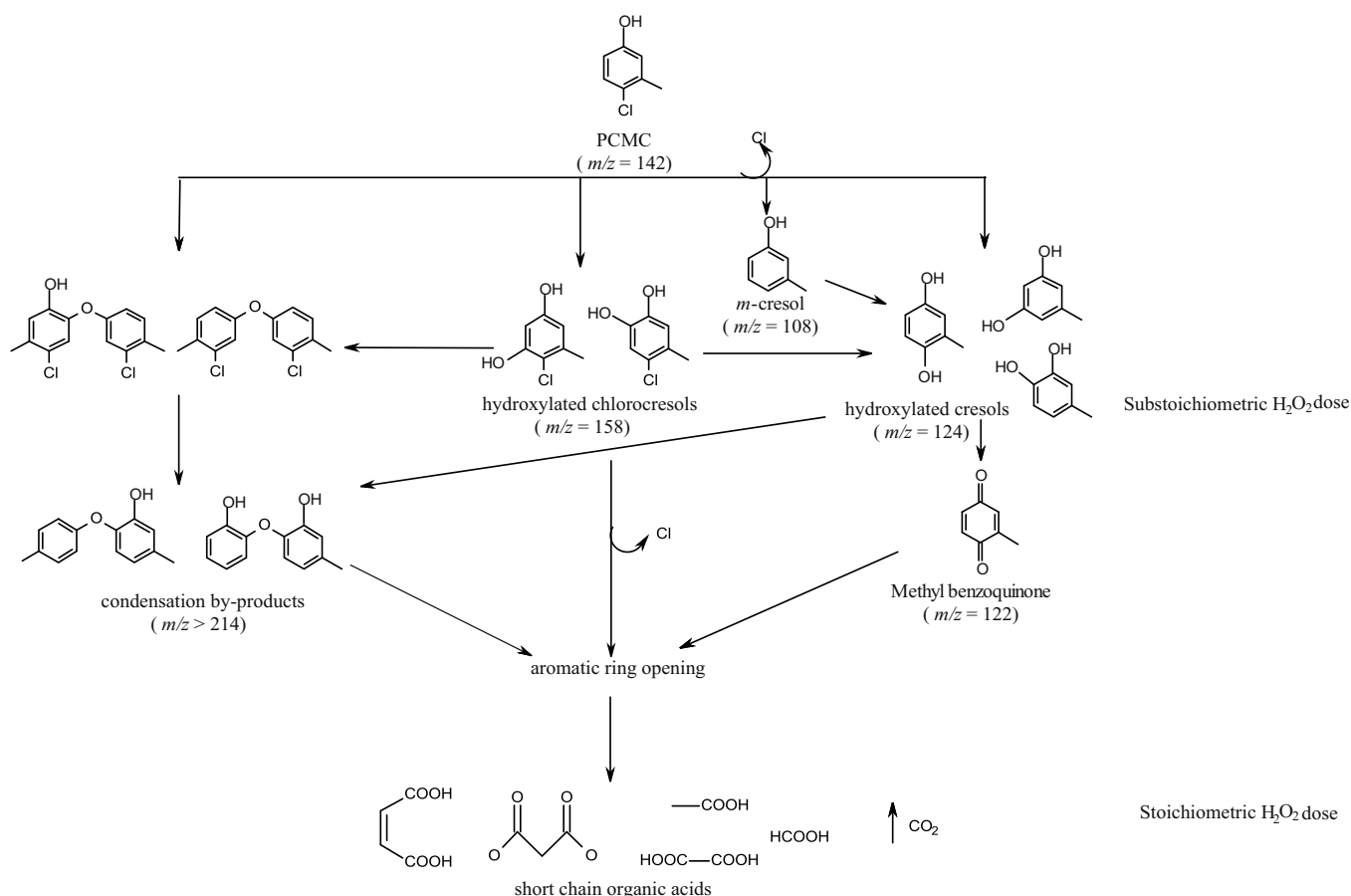
Table 4
Reaction byproducts identified by GC/MS from the CWPO oxidation of PCMC and *m*-cresol ([pollutant]$_0$ = 1000 mg/L [AlFe25]$_0$ = 1 g/L; [H_2O_2]$_0$ = 20% of the stoichiometric dose).

m/z	PCMC CWPO by-products	m/z	m-cresol CWPO by-products
107	*m*-cresol	82	3-methyl-furan
122	2-methyl-p-benzoquinone	107	Residual *m*-cresol
124	3-methyl-1-4-benzendiol	122	2-methyl-p-benzoquinone
142	Residual PCMC	124	Hydroxylated cresols

Fig. 7. Reaction scheme for CWPO oxidation of PCMC with the AlFe25 catalyst.

on the nature of those species, a CWPO experiment was performed with a higher initial concentration of PCMC (1000 mg/L), under frankly substoichiometric doses of H_2O_2 (20%) with the AlFe catalyst. More than 90% of PCMC and 65% of H_2O_2 were converted upon 8 h reaction time. However, TOC reduction achieved less than 20% and the chlorine balance closure was fairly low ($\approx$33%). The TOC calculated from the identified species was only 55% of the experimentally measured. These results confirm the existence of important amounts of unidentified chlorinated species. Therefore, the CWPO effluent was further analyzed by GC/MS. The identified species are collected in Table 4 where there have been included also the obtained from a similar CWPO experiment using as starting compound *m*-cresol, the main product from PCMC hydrodechlorination. The main reaction by-products were formed by hydroxylation of the aromatic ring giving rise to hydroxylated cresols (m/z = 124) and methyl benzoquinones (m/z = 122), which is in agreement with previous works dealing with the oxidation of PCMC by different AOPs [41–43]. Those species include highly toxic and carcinogen compounds [44,45] and thus, their complete removal from the oxidation effluent is crucial. Condensation by-products such as aromatic dimers were not detected, which could be due to their adsorption on the catalyst surface since the color of the solid evolved from light orange to dark brown after reaction. The formation of methyl-furan may proceed from 4-methyl-catechol oxidation as reported by other authors [46,47].

To gain further insights on the reaction pathways of PCMC oxidation, homogeneous Fenton experiments under the same operating conditions were also carried out. Now, the rate of PCMC disappearance increased dramatically (90% conversion was reached in about 5 min) but the maximum TOC reduction was also around

20% and more than 70% of the measured TOC remained unidentified while the closure of chlorine balance was again below 40%. A brownish color developed in the reaction medium and a dark solid residue was recovered after evaporation. Previous studies [13,14,48] have reported on the formation of aromatic condensation by-products, including chlorinated species, upon Fenton oxidation of chlorophenols and chlorobenzene. The analysis of the byproducts from homogeneous Fenton oxidation of PCMC and *m*-cresol suggests the formation of condensation by-products (see supporting information).

From the results obtained the reaction pathway of Fig. 7 is proposed for CWPO of PCMC. The oxidation of PCMC mainly led to the formation of hydroxylated chlorocresols and cresols. Condensation by-products were also formed under substoichiometric operating conditions. Those species were further attacked by hydroxyl radicals leading to the formation of short-chain organic acids.

3.5. Treatment of PCMC by combined HDC and CWPO

The formation of the highly toxic chlorinated species so far described represents a serious drawback for the application of direct oxidation to the abatement of PCMC and related chlorine-bearing pollutants. Combination with a previous dechlorination step can provide an effective and safe solution.

The combination of HDC and CWPO was carried out with the bimetallic catalyst impregnated with Pd and Fe (IMPFe-Pd). As shown before, this bimetallic catalyst presents a high dispersion of the active phase favouring a high HDC activity. Also it showed a remarkable stability under basic pH, where very low iron leaching occurred during the HDC step. Fig. 8 shows the results obtained
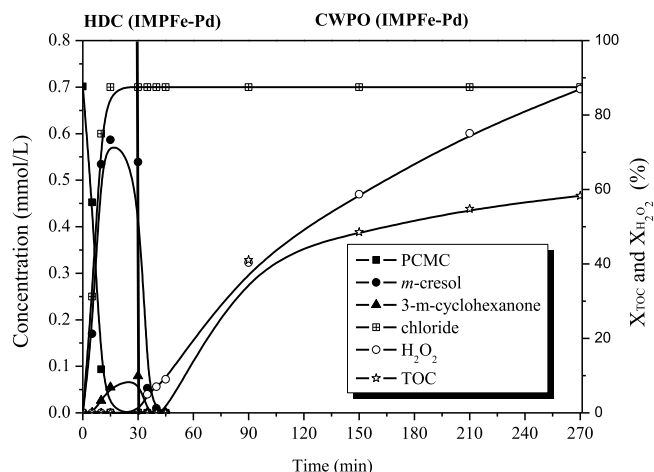
Fig. 8. Combined HDC + CWPO treatment (25 °C, 1 atm, $pH_{0(HDC)} = 10$, $pH_{(CWPO)} = 3.5$, $Q_{H2} = 50$ NmL/min, [IMPFe-Pd] = 1 g/L, $[PCMC]_0 = 0.7$ mmol/L, $[H_2O_2]_0 =$ stoichiometric).

upon HDC (at pH 10) of PCMC followed by CWPO (with the stoichiometric H_2O_2 dose relative to the HDC products). The HDC step extended for 30 min since that reaction time was enough to achieve complete dechlorination. The main reaction product of this step was m-cresol (selectivity >85%). After the HDC step, the pH of the reaction medium was adjusted to 3.5 with diluted HNO_3 and the stoichiometric H_2O_2 dose was added to start the CWPO step. This allowed complete conversion of m-cresol in 15 min, with 60% TOC reduction after 4 h reaction time. The Fe leached from the catalyst in this combined treatment reached 2.5 mg/L in the HDC step and 4.9 mg/L at the end of the experiment, representing 6.6% of the initial Fe load.

3.5.1. Combined treatment with monometallic catalysts

The combination of HDC and CWPO using different monometallic catalysts for each stage (HDC: Pd-1, CWPO: AlFe25) was also investigated. Fig. 9 shows the results obtained. The HDC step (at pH 10) allowed complete dechlorination in somewhat more than 1 h. Then, the Pd-1 catalyst was separated by filtration, the pH adjusted to 3.5 and the AlFe25 catalyst was added, as well as H_2O_2, this last at the theoretical stoichiometric amount for complete mineralization of the m-cresol from the HDC step. After 3 h of CWPO, around
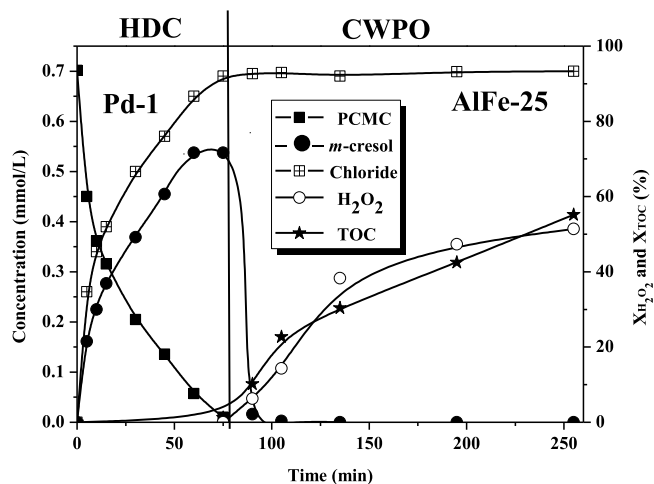
55% mineralization was achieved while only slightly more than 50% H_2O_2 was decomposed, much less than with the bimetallic catalyst (see Fig. 8). Significantly lower Fe leaching was observed (1.1 mg/L, representing 1.5% of the initial iron load).

Other works dealing with the combination of HDC and CWPO with Pd-γAl_2O_3 and Fe-γAl_2O_3 as catalysts for the elimination of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol can be found in the literature. The HDC step showed fairly similar behaviour at 30 °C and the CWPO step achieved 70% mineralization using two fold the catalyst concentration of this work and higher temperature (50 °C) [15]. The sequential use of monometallic catalysts allowed complete PCMC dechlorination and 55% mineralization at ambient conditions, with low Fe leaching, making preferable the use of this approach with respect to the system based on bimetallic catalysts.

4. Conclusions

Monometallic and bimetallic catalysts supported on pillared clays have been prepared and tested in the sequential HDC-CWPO treatment of PCMC under ambient conditions (25 °C, 1 atm). The Pd- and Rh-containing catalysts tested in HDC allowed complete dechlorination, leading to m-cresol and 3-methyl-cyclohexanone as reaction products in both cases, in addition to 3-methyl-cyclohexanol with the Rh one. On the other hand, direct CWPO with monometallic Fe catalysts gave rise to some hazardous chlorinated by-products thus hindering the direct application of the oxidation treatment under substoichiometric oxidant doses.

The combination of HDC and CWPO has proved to be an effective alternative for the treatment of PCMC, as it allowed complete dechlorination and a fair mineralization (55%), being the final products short-chain organics acids without significance in terms of ecotoxicity. With regard to the stability of the catalysts, the application of independent monometallic catalysts for each reaction step is preferable to a single bimetallic one. However, further research is needed to learn more in depth on the stability of the bimetallic catalysts upon long-term experiments, since this is a crucial issue regarding potential application.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.05.052.

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Fig. 9. Combined HDC + CWPO treatment with separated catalysts (25 °C, 1 atm, $pH_{0(HDC)} = 10$, $pH_{(CWPO)} = 3.5$, $Q_{H2} = 50$ NmL/min, [catalyst (Pd-1 for HDC and AlFe25 for CWPO)] = 1 g/L, $[PCMC]_0 = 0.7$ mmol/L, $[H_2O_2]_0 =$ stoichiometric).

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